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Benchmark thermodynamic properties of methylanisoles: Experimental and theoretical study

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ABSTRACT

Accurate standard molar enthalpy of formation values in the liquid phase can be obtained by combining high-level quantum chemistry values of gas-phase enthalpies of formation with experimentally determined enthalpies of vaporisation. The procedure is illustrated for 2-, 3-, and 4-methyl-anisoles. Using the W1-F12 and G4 quantum-chemical methods, the gas-phase enthalpies of formation of these compounds at $T = 298.15$ K were computed. Molar enthalpies of vaporisation for these isomers were measured by the transpiration method. Combining the experimental and the high-level *ab initio* values, the standard molar enthalpies of formation in the liquid phase for all three isomers were derived and compared with those determined for 2- and 4-methyl-anisoles by using combustion calorimetry.

1. Introduction

Electrophilic aromatic substitution is one of the most relevant synthetic pathways available for benzene rings, and the kind and location of the ring substituents exert a significant control on both reactivity and region-selectivity of this reaction [1]. A deep understanding of the substituent effect and its influence on the reactivity of aromatic systems requires the knowledge of their thermochemical properties, namely their standard enthalpies of formation, $\Delta_f H^\circ_m$ [2]. Although these values are known for a fairly large number of organic molecules [3,4], there are still important gaps for substituted benzenes, hindering a quantitative understanding of the reactivity of aromatic systems.

The three methylanisoles (figure 1) constitute one such gap.

Alkyl and alkoxy groups are far from being uncommon benzene substituents, yet much is unknown regarding the thermochemistry of even the simplest alkoxy-alkylbenzenes. While 3-methylanisole has been previously studied [3,5], the data for the whole series is required to fully understand the effect of these substituent groups. We therefore set out to perform a benchmark thermochemical study of the methylanisoles. For this purpose, their vaporisation enthalpies were obtained from their vapour pressures, measured using the transpiration method [6], and the enthalpies of formation of 2- and 4-methylanisole in the liquid phase were determined by combustion calorimetry [2,7]. When combined, these data yielded the gas-phase enthalpy of formation for each compound, which were also obtained from high-level *ab initio* calculations.

In a previous work [8] we posited that quantum chemical methods have now reached a precision and accuracy that, for small- to mid-sized molecules, matches that of experimental techniques. We further stated that this notion implies that, when condensed phase data are unavailable, these properties can be obtained by combining theoretical gas-phase enthalpies of formation with experimental vaporisation or sublimation enthalpies. Comparison of the experimental and theoretical data provides a further test to the reliability of this approach.

2. Materials and methods

2.1. Materials

Samples of methylanisoles of commercial origin (see table 1) with 0.99 mass fraction purity were further purified by fractional distillation with a spinning-band column in vacuum. No impurities

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